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The Collection and Determination of Chromium in an Urban Atmosphere

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Introduction

In 1958 the National Air Sampling network of the U.S. Public Health Service disclosed that the average chromium concentration of 71×10^{-3} micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) in the air of Baltimore City was ten times the national average for the period 1954-1957.¹ Also, the maximum chromium concentration ($290 \times 10^{-3} \mu\text{g}/\text{m}^3$) for the entire network was collected in Baltimore City. Because of the association of chromium compounds with cancer,^{2,3} a more detailed investigation was undertaken in 1959 by the Baltimore City Health Department. It is the purpose of this paper to describe some of the air-borne chromium concentrations resulting from this study⁴ and to detail the chemical method of analysis used.

Sample Location, Collection, and Results

Although several probable sources of emission of chromium compounds were known to exist in Baltimore, a sampling station was established closest to a chrome chemical processing plant because of the health experience among its workers. In addition, it was hoped that with scheduled sampling, offending operations might be singled out and corrective measures instituted.

Over a period of two months (July-August, 1959) 736 atmospheric dust samples

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were obtained on Whatman So. 4 filter paper tape by means of the A.I.S.I. Automatic Smoke Sampler.⁵ The machine was adjusted to a two-hour sampling cycle, thus providing one-inch diameter dust spots each representing a known volume of air previously determined by calibration. The sampled air volume for a two-hour period was approximately 0.7 cubic meter. The strip of tape containing one week's samples (84 spots) was submitted weekly for analysis. The details of the procedure outlined here are based on this actual work load.

A portion of the data collected appears in Figure 1. By plotting the concentration against the daily sampling interval, the graph shows not only the average concentrations for the two-hour periods by a solid black wide line but also the maximum concentrations for all of the respective two-hour periods by a narrow line. It is noted that the two curves are quite similar and that the maximum concentration appeared between 1315 and 1515 hours, while the minimum concentration was between 0315 and 0715. The major operations of the plant were performed between 0700 and 1600 hours. There was a quick build-up of concentrations at the sampling site located about 700 feet from the plant as the major daily operations began. The fall-off after the operations ceased was of a gradual nature.

Further use of the data appears in Figure 2 where wind direction is plotted against average and peak concentrations as well as against the number of samples. The maximum concentrations, both average as well as peak, appeared when the wind was from the southeast quadrant, i.e., from the plant to the sampling station. The dotted curve is indicative of the wind directions for the en-

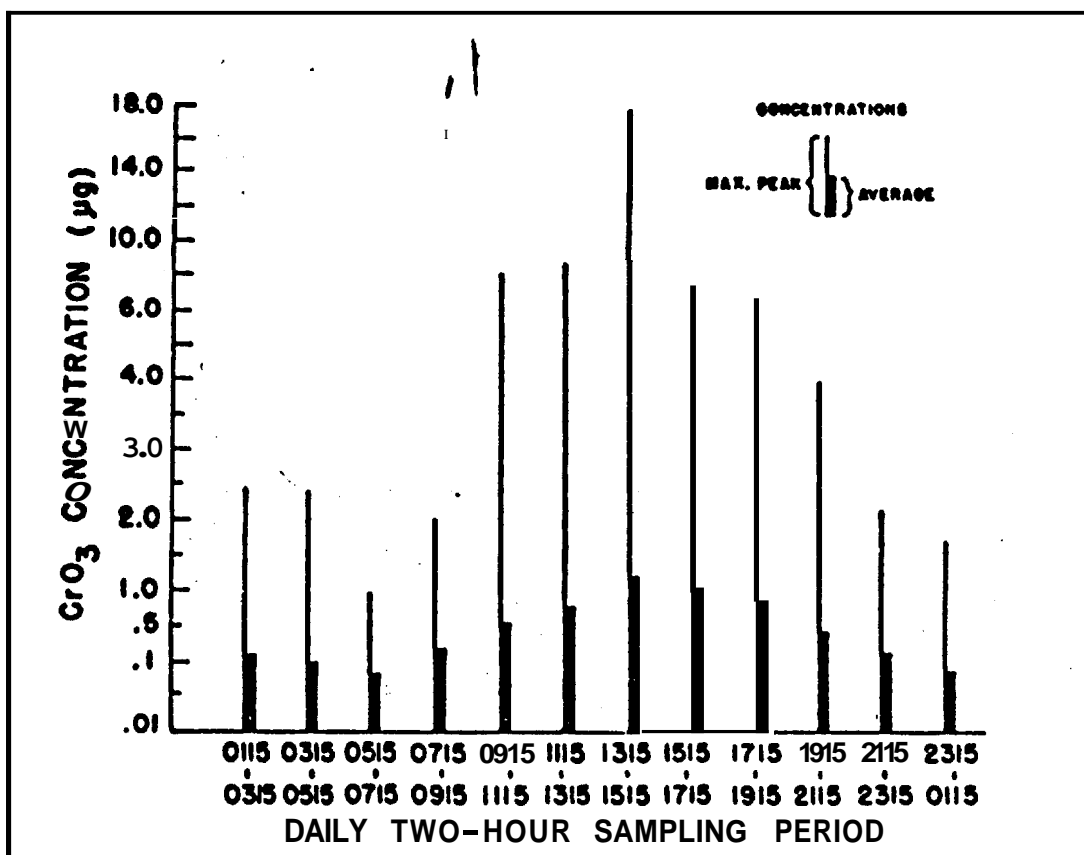
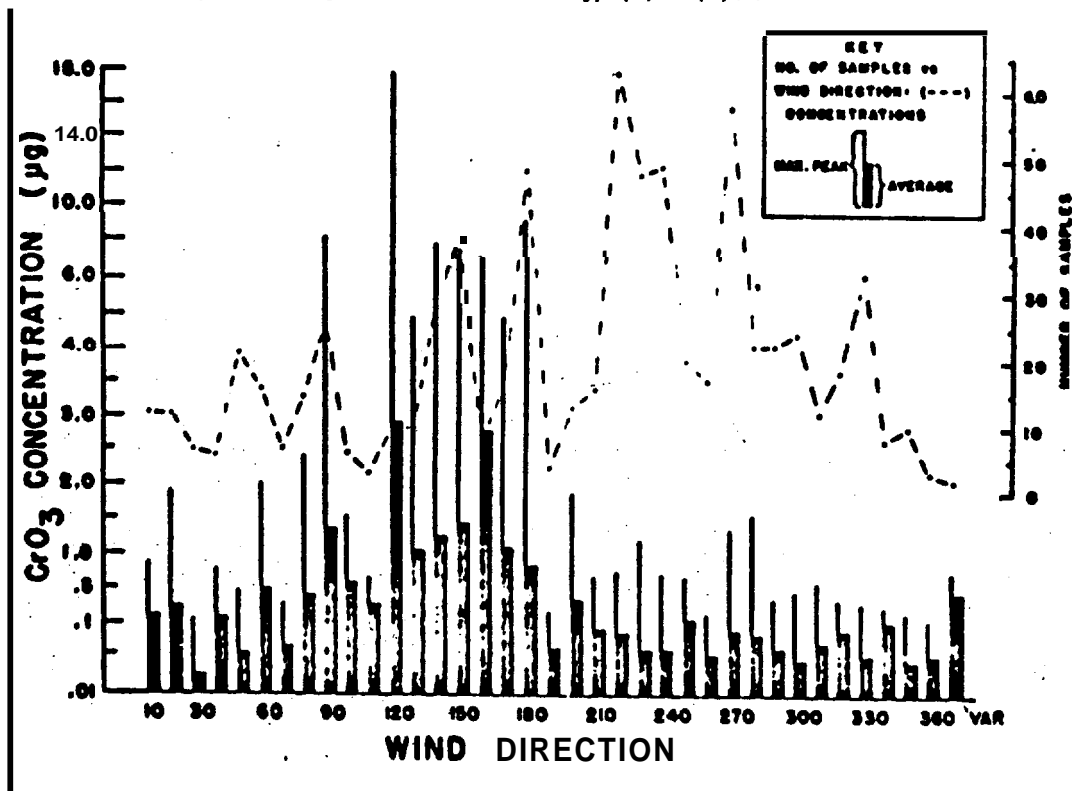


Fig. 1.—Atmospheric chrome dust study, 7/1/59-9/1/59. Daily two-hour sampling period.

Fig. 2.—Atmospheric chrome dust study, 7/1/59-9/1/59. Wind direction.



five sampling period between July and August, inclusive. The wind was predominantly from the south-southwestern portion of the compass. Another interesting facet appears in that there is a background of chromium of the order of $0.08 \mu\text{g}$. of chromic acid anhydride, CrO_3 , for a two-hour sample. This is equivalent to $60 \times 10^{-3} \mu\text{g}$. Cr/m^3 (chromium as metal) and is in reasonable agreement with the average chromium concentration of $70 \times 10^{-3} \mu\text{g}/\text{m}^3$ of air reported for the 1957 network for the Baltimore Station.

Method for the Determination of Chromium

Samples, cut from filter paper tape, are dry ashed in Pyrex test tubes and then fused with sodium peroxide, leached with water, acidified, and treated with *s*-diphenylcarbazide. The pink-to-violet *c d* is read visually against freshly prepared standards. This color reaction is extremely sensitive for hexavalent (chromate) chromium. The test, as a result of the peroxide fusion, yields values for total chromium only. No attempt is made to differentiate hexavalent and trivalent chromium.

This method is applicable in the range of 0 to $10 \mu\text{g}$. CrO_3 (0.0 to $5.2 \mu\text{g}$. Cr). It will detect $0.1 \mu\text{g}$. of chromium (as CrO_3) and will measure in excess of $0.2 \mu\text{g}$. CrO_3 with an accuracy of 10% to 20%. The total reagent blank is of the order of $0.1 \mu\text{g}$. (equivalent) CrO_3 . The method is well adapted to the mass handling of atmospheric dust samples. Groups of 80-100 samples, plus the necessary standards, controls, and blanks, may be handled with comparative ease.

Equipment and Reagents

Test tubes for ashing, fusion, etc. (Corning No. 9820) without rim, 13 mm. O.D. \times 100 mm.

Protective glass tubes, 17 mm. O.D. \times 90 mm., without rim.

Aluminum furnace rack (Fig. 3) for test tubes.

Glass spatula made by softening in the flame one end of a Pyrex glass rod, 5 mm. \times 150 mm., and flattening longitudinally with wide-tipped pliers.

Muffle furnace with rheostat, pyrometer, and thermocouple. (Hoskins Electric Muffle Furnace, FD 204.)

All reagents are of analytical grade.

Sodium peroxide, Na_2O_2 , granular, 35-40 mesh, calorific grade.

Sulfuric acid, H_2SO_4 , approximately 18 N: Cautiously add 20 ml. concentrated H_2SO_4 , 36 N, to 20 ml. of distilled water. Cool to room temperature.

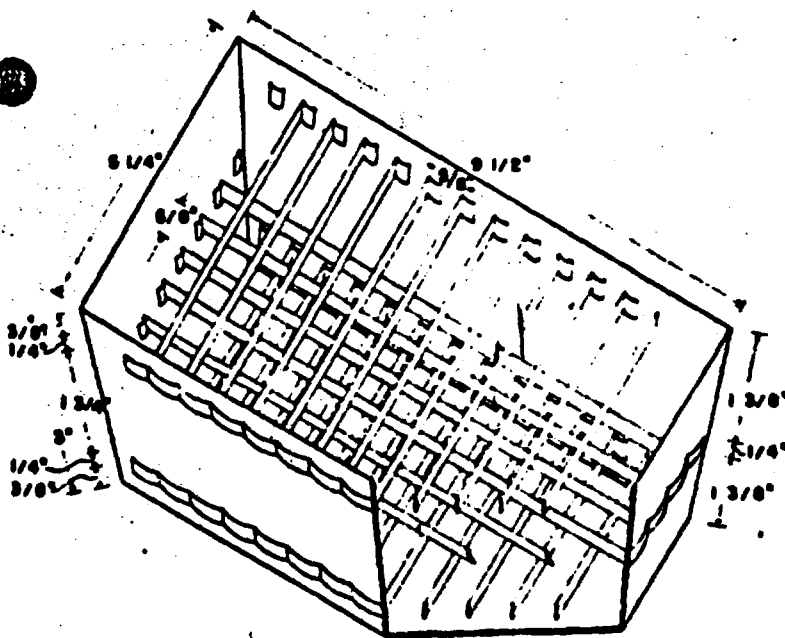


Fig. 3.—Aluminum rack.

DESCRIPTION OF ALUMINUM DIVIDERS

24 STRIPS, EACH $6 \frac{1}{2}'' \times \frac{1}{4}'' \times \frac{1}{32}''$

6 STRIPS, EACH $10 \frac{3}{4}'' \times \frac{1}{4}'' \times \frac{1}{32}''$

s-Diphenylcarbazide solution: Dissolve 0.4 gm. phthalic anhydride in 8.0 ml. 95% ethyl alcohol. Add 50 mg. powdered s-diphenylcarbazide (Eastman Organic Chemicals No. 618) and dissolve completely. Make up to 10 ml. with 95% ethyl alcohol. Store in a brown bottle in the refrigerator. The solution will be satisfactory for three or four days. In the range of 0.0 to 0.5 $\mu\text{g. CrO}_3$ per sample a water-clear reagent free of yellow color is necessary.

Standard chromium solutions: Prepare a stock standard by dissolving 0.1471 gm. potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$ (National Bureau of Standards Sample No. 136a), in distilled water and make up to one liter. Dilute 25 ml. of the stock standard to 250 ml. to prepare the working standard in which 1 ml. = 10 $\mu\text{g. CrO}_3$. (If it is preferred to work in terms of Cr, use 0.2829 gm. $\text{K}_2\text{Cr}_2\text{O}_7$ to prepare one liter of stock standard and proceed with a 1:10 dilution to prepare the working standard in which 1 ml. = 10 $\mu\text{g. Cr}$.) Store these solutions in polyethylene bottles.

Analytical Procedure

Identify the dust spots to correspond with the exact time of sampling. Cut each spot from the tape, fold the paper circle twice (dust side in) and transfer it to a Pyrex glass test tube (13 mm. X 100 mm.) supported in the aluminum rack. Place the rack of tubes in a cool muffle furnace. Adjust the rheostat so that the furnace will reach 600 C and will be held at this temperature in overnight heating. When ashing is complete, remove the rack of tubes and allow to cool to room temperature. Turn off the furnace and allow it to cool.

To the ash of each sample in its tube add 30-40 mg. Na_2O_2 with the small glass spatula. (Excess Na_2O_2 will yield unsatisfactory turbid solutions.) Mix by gently capping the bottom of the tube. Return the tubes in the aluminum rack to the cool muffle furnace. Heat as rapidly as possible to 550 C, then remove the rack of tubes and allow to cool to room temperature. Transfer the tubes to regular open-base test tube racks for subsequent chemical treatment and color matching. Insert each tube containing the fused mass into a protective outer glass test tube (17 mm. X 90 mm.). This outer tube is kept in place for the remainder of the test. The reaction tubes may crack at the site of the fusion but will usually remain intact after the completion of the test, after which they are discarded. Rinse down the sides of the reaction tube with 3.0 ml. of distilled water. Cover and allow the fusion to leach overnight.

Standards, blanks, and controls are treated concurrently with the samples. For these, blank ash fusions are prepared by transferring a folded one-inch circle cut from unused Whatman No. 4 filter paper tape to each of 15 Pyrex test tubes (13

mm. X 100 mm.) for each 36-40 samples. Ash and fuse with sodium peroxide as described above. Place the tubes, each with a protective outer tube, in regular open-base test tube racks. Transfer 0.00, 0.01, 0.02, 0.03, 0.05, 0.07, 0.10, 0.20, 0.30, 0.50, 0.70, and 1.00 $\mu\text{l.}$ of standard chromium solution (1 ml. = 10 $\mu\text{g. CrO}_3$) to each of 12 blank ash fusion tubes. Standard chromium solution up to 0.05 ml. should be added with a 50 X 10 mm. pipet. The standards represent 0.0 to 10.0 $\mu\text{g. CrO}_3$ per tube. Dilute to 5.0 ml. with distilled water added carefully by pipet to wash clean the sides of the test tube. Cover and allow to leach overnight. A total reagent blank and a positive control should be run with each lot of samples.

To each tube (i.e., samples, control, blank, and standards) add three drops of 18 N H_2SO_4 . Carefully disperse the leached mass with a glass stirring rod. Avoid contact with the base of the tube to prevent breakage. Correctly acidified solutions will turn congo red paper blue-black. Add two drops of s-diphenylcarbazide solution to one-half of the number of tubes containing samples, then to each of the 12 standards, and finally to the remaining sample-containing tubes, including blank and control. (To avoid low readings from fading color in samples and standards, do not add s-diphenylcarbazide to more than 36-40 samples at a time. A fresh set of color standards is needed for each such group of samples.) Mix carefully with a flat-head glass rod. After 5-10 minutes, match the samples against the standards viewing vertically in the tube held against a white background preferably in north light. Samples containing less than 0.5 $\mu\text{g. CrO}_3$ per tube should be read within 15 minutes following color-reagent addition. If the color produced in a sample exceeds the highest standard, dilute an aliquot of the treated sample using as the diluent the acidified leach of a reserve blank ash fusion. Add one or two drops of s-diphenylcarbazide solution, mix, and re-read.

Calculation

A typical calculation of results is shown, based upon the following data: two-hour sampling at 13.1 cfm produced a dust spot representing 26.2 cu. ft. of air. Set chromium in the dust sample, as read against standards and deducting 0.1 $\mu\text{g. CrO}_3$ blank, was 0.2 $\mu\text{g. CrO}_3$. (0.2 $\mu\text{g. CrO}_3$ X 33.3 cu. ft.) + 26.2 cu. ft. air sample = 0.27 $\mu\text{g. CrO}_3/\text{m}^3$, equivalent to $140 \times 10^{-5} \mu\text{g. Cr}/\text{m}^3$.

Comment (Analysis)

Interferences: Only hexavalent molybdenum gives a similar violet color with

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p-diphenylcarbazide in mineral acid solution, but reacts much less sensitively than chromium. Trident iron was not present in sufficient quantity on dust spots to interfere. To avoid severe contamination by iron and chromium from scaling of steel or stainless steel racks, these were not used in furnace ashing and fusion steps of the method. Instead, an aluminum rack (Fig. 3) was fashioned to accommodate 91 test tubes. Narrow strips of aluminum sheet ($1\frac{1}{4}'' \times 1\frac{1}{2}''$ and cut to appropriate lengths) were inserted in slots tapped into the sides and ends of an aluminum baking pan ($9\frac{1}{2}'' \times 5\frac{1}{4}'' \times 3''$). A few Pyrex glass rods, 5 mm. \times 150 mm. placed equidistantly and laterally on the floor of the muffle furnace, facilitated movement of the rack of tubes in and out of the furnace. Contamination of samples with particles of refractory material from the walls or door of the muffle furnace must be avoided. These refractories may be chrome-bearing. In removing tube from the hot furnace, avoid contamination with particles of glove asbestos which may also be chrome-bearing.

Recovery of CrO₃ Added to Blank Filter Paper Circles (Control Samples)

$\mu\text{g CrO}_3$ Added	$\mu\text{g CrO}_3$ Found (Corrected for Blank)	Per Cent Recovery
0.1	0.08	80.
0.2	0.21	105.
0.3	0.26	86.
0.4	0.36	90.
0.5	0.46	92.
1.0	1.13	113.
1.5	1.46	97.
2.0	2.06	103.
5.0	5.00	100.
10.0	9.98	99.

Recovery: Typical recovery values for chromium (as $\mu\text{g. CrO}_3$) are shown in the Table.

Summary

A method is described for the detection and measurement of microgram quantities of chromium in large numbers of atmospheric dust samples collected on filter paper tape. The method was applied to a study of chromium in an urban atmosphere.

Bureau of Laboratories, Baltimore City Health Department.

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